



# Photocatalytic ammonia synthesis from nitrate reduction on nickel single-atom decorated on defective tungsten oxide

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## ABSTRACT

Photocatalytic reduction of waste nitrate (NO<sub>3</sub><sup>-</sup>) into value-added ammonia (NH<sub>3</sub>) under ambient conditions has enormous advantages over the Haber-Bosch process. However, weak adsorption capacity and low efficiency of photocatalysts limit its large-scale application. Here, Ni single-atom (SA) on defective WO<sub>3</sub> (Ni/H<sub>x</sub>WO<sub>3-y</sub>) hybrids with abundant oxygen vacancies (OVs) are synthesized by a facile H-spillover process, which exhibits a high NH<sub>3</sub> rate of 10.5 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and 98.26 % NH<sub>3</sub> selectivity. In situ characterizations and theoretical calculations demonstrate the activity mainly derives from the synergetic effect of OVs and Ni SAs. That is, (1) photogenerated electrons and adsorbed NO<sub>3</sub><sup>-</sup> transfer from OVs to Ni SAs; (2) the strong hybridizations of Ni 3d - O 2p orbitals of NO<sub>3</sub><sup>-</sup> accelerate electron transfer from Ni SAs to NO<sub>3</sub><sup>-</sup>; (3) Ni SAs effectively reduce the free energy of the rate-limiting step (NO<sub>2</sub><sup>\*</sup> → NO<sup>\*</sup>) of H<sub>x</sub>WO<sub>3-y</sub>. In simulated wastewater, the durable performance of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids proves great potential in industrial applications.

## 1. Introduction

Ammonia (NH<sub>3</sub>) is regarded as an essential chemical and a potential carrier of hydrogen energy [1–3]. Currently, industrial-scale NH<sub>3</sub> synthesis relies heavily on the Haber-Bosch process requiring severe operating conditions of high temperatures and pressures [4,5]. Additionally, nitrate (NO<sub>3</sub><sup>-</sup>) pollutants in nature pose a serious danger to human health [6]. Although several industrial strategies for treating NO<sub>3</sub><sup>-</sup> wastewater have been adopted, such as ion exchange and microbial transformation, their practical applicability is restricted by their expensive cost and/or complicated processes [7,8]. Hence, the promising strategy for photocatalytic NH<sub>3</sub> synthesis from NO<sub>3</sub><sup>-</sup> reduction at ambient conditions has attracted much attention recently due to the advantages of sustainability, cleanliness, and low energy consumption [1,9–12]. Moreover, it should be noted that some organic substances, such as alcohols and aldehydes, which can serve as hole scavengers in the photocatalytic process, are also widely dispersed in NO<sub>3</sub><sup>-</sup>-containing wastewater [9,12]. Therefore, photocatalytic synergistic reduction of NO<sub>3</sub><sup>-</sup> for NH<sub>3</sub> synthesis and removal of organic matter is of great importance for the treatment of water pollution and development of sustainable energy economy.

However, weak adsorption capacity for NO<sub>3</sub><sup>-</sup> and low efficiency for NH<sub>3</sub> synthesis of photocatalysts limit their large-scale application [13].

To increase efficient active sites and improve carrier separation efficiency of catalysts on photocatalytic NO<sub>3</sub><sup>-</sup> reduction [14,15], many effective strategies, such as defect structure construction [16], cocatalyst loading [17], and band gap engineering [18], have been proposed to obtain highly selective products [19]. Notably, constructing oxygen vacancies (OVs) on semiconductor surfaces is an effective method for enhancing photocatalytic activity [20]. The localized surface plasmon resonance (LSPR) of transition metal oxides with plenty of OVs is capable of inducing a large number of localized electrons and has been shown to be very effective in the adsorption and activation of small molecules such as N<sub>2</sub> [21,22] and CO<sub>2</sub> [23,24]. Yamashita's group reported that abundant localized electrons induced by sustained OVs on 2D H<sub>x</sub>MoO<sub>3-y</sub> nanosheets can greatly promote charge-carrier separation in the visible region [25], ultimately improving photocurrent responsiveness and photocatalytic activity. As another n-type semiconductor, tungsten trioxide (WO<sub>3</sub>) has a wide bandgap (2.8 eV) [26]. The heavily doped non-stoichiometric counterpart (H<sub>x</sub>WO<sub>3-y</sub>) with abundant OVs has an extensive solar absorption region induced by LSPRs, which can

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effectively adsorb and activate  $\text{NO}_3^-$ . On the other hand, compared with metal nanoparticles (NPs), single-atom (SA) catalysts exhibit effective catalytic activity and provide an atomic-scale perspective of understanding the reaction mechanism, which have ultra-high atom utilization and unique electronic structure [27–30]. Moreover, due to the unique spatial isolation property, the monoatomic active site can effectively avoid  $\text{N}^*-\text{N}^*$  coupling required for  $\text{N}_2$  and  $\text{N}_2\text{O}$  [31–33]. Currently, it has been reported that non-noble metal Ni SA plays an important role in binding  $\text{H}^*$  [34] and has a strong adsorption effect on important intermediates such as  $\text{NO}_2^*$  and  $\text{NH}_2^*$  [35,36]. Therefore, considering the advantages of OVs and SAs in  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ , it is significant and necessary to obtain Ni SAs decorated on plasmonic  $\text{H}_x\text{WO}_{3-y}$  (denoted as  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$ ), which are expected to show synergistic multilevel coupling effects for further improving  $\text{NH}_3$  synthesis efficiency.

In this work, we report Ni SAs decorated on heavily hydrogen-doped  $\text{WO}_3$  ( $\text{Ni}/\text{H}_x\text{WO}_{3-y}$ ) hybrids by a facile H-spillover route.  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids with abundant OVs exhibit strong visible light absorption with the LSPR peak at around 550 nm, which greatly improves the utilization of full-spectrum light. Relative to pristine  $\text{WO}_3$ ,  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids with dual active sites of OVs and Ni SAs effectively promote photocatalytic  $\text{NO}_3^-$  reduction under ambient conditions with  $\text{NH}_3$  yield of  $10.5 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  and 98.26 %  $\text{NH}_3$  selectivity in a certain leading position in the area of  $\text{NH}_3$  synthesis. More importantly, in situ electron paramagnetic resonance (EPR), in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFT), and density generalized function theory (DFT) calculations successfully reveal the reaction mechanism and the origin of high activity of  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids. In addition, the simulation application of  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids in real polluted water bodies provide a promising strategy with industrial development prospects.

## 2. Experimental section

### 2.1. Synthesis of $\text{Ni}/\text{H}_x\text{WO}_{3-y}$ hybrids

In a typical synthesis, 400 mg of commercial  $\text{WO}_3$  was dispersed in 50 mL of aqueous solution. Subsequently, 35 mg of polyvinylpyrrolidone K-30 (PVP) and an amount of  $\text{NiCl}_2$  solution were injected into the reaction solution and stirred for 6 h under magnetic stirring. The Ni percentage was maintained at 0.5 wt%. Finally, the powder ( $\text{Ni}/\text{WO}_3$ ) was calcined in a tube furnace at  $500^\circ\text{C}$  for 3 h under hydrogen atmosphere.

### 2.2. Material characterization

The samples were characterized by various measurements, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman, nitrogen adsorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), X-ray absorption fine structure (XAFS),  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR), UV/Vis-NIR diffuse reflectance, photocurrent response, impedance curves, Mott-Schottky curves, PL spectra, time-resolved fluorescence decay spectra, Fourier-transform infrared spectra (FT-IR), electron paramagnetic resonance (EPR), in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS), and in situ electron paramagnetic resonance (in situ EPR). The detailed operation procedures of the above characterizations can be found in Supporting Information.

### 2.3. Catalytic performance measurements

The catalytic test procedures including catalytic activities for photocatalytic  $\text{NO}_3^-$  reduction, apparent quantum efficiency (AQE), and long-term stability are shown in Supporting Information in detail.

### 2.4. DFT calculation detail

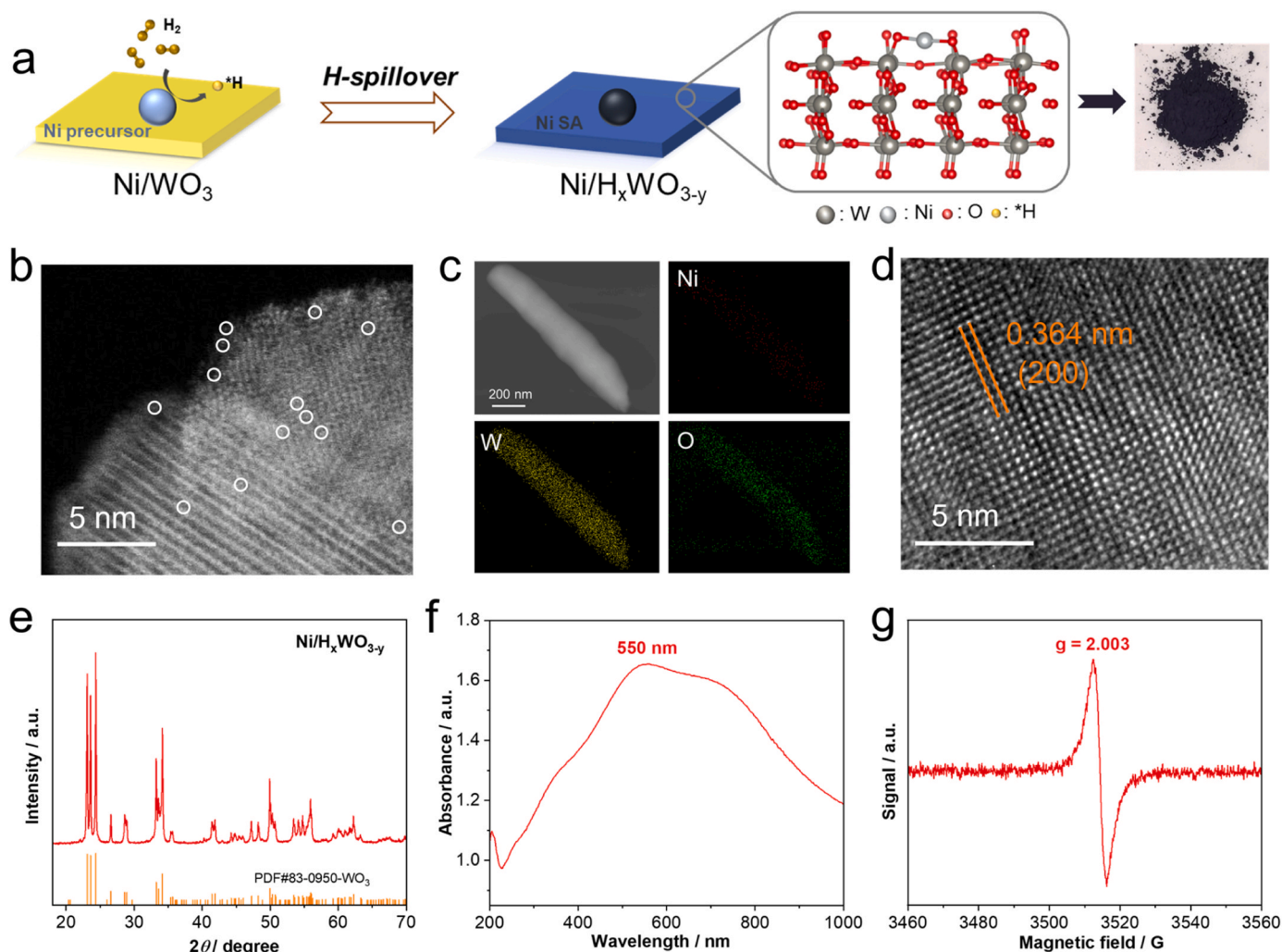
The density functional theory (DFT) calculations were conducted with the Vienna ab initio simulation package (VASP). The model structures were optimized using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation plus the Hubbard model (GGA), with 400 eV of kinetic cutoff energy and a k-point mesh of  $2 \times 2 \times 1$  in Monkhorst-pack scheme. The computational hydrogen electrode method was applied to calculate the adsorption free energies. More details of computational methods can be found in Supporting Information.

## 3. Results and discussion

### 3.1. Structure and morphology of $\text{Ni}/\text{H}_x\text{WO}_{3-y}$ hybrids

Fig. 1a displays the synthetic process of Ni SAs decorated on heavily hydrogen-doped  $\text{WO}_3$  by a facile H-spillover process. The in-situ formed Ni SAs cause a rapid dissociation of  $\text{H}_2$  to dopants ( $\text{H}^*$ ). Then, free electrons and  $\text{H}^*$  migrate to  $\text{WO}_3$ , which leads to the partial reduction of  $\text{W}^{6+}$  [22,37]. The scanning electron microscopy (SEM) images (Fig. S1) show that  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids and reference samples ( $\text{WO}_3$ ,  $\text{Ni}/\text{WO}_3$ , and  $\text{H}_x\text{WO}_{3-y}$ ) maintain rod-like structures of  $\text{WO}_3$ . The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image (Fig. 1b) of  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids exhibits that no Ni NPs but only isolated Ni SAs labeled with white circles are clearly observed on  $\text{H}_x\text{WO}_{3-y}$ . Energy dispersive X-ray (EDX) spectrometry (Fig. 1c) show that W, O, and Ni elements are uniformly distributed on  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids. The high-resolution transmission electron microscopy (HRTEM) image of the  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids (Fig. 1d) indicates clear lattice fringes with interplanar spacings of 0.364 nm, corresponding to the (200) plane of  $\text{WO}_3$ . Notably, a disordered surface layer with a thickness of about 1 nm can be observed in  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids (Fig. S2), which mainly stems from the introduction of OVs during H-spillover process [38–40]. The adsorption-desorption of  $\text{N}_2$  analysis (Fig. S3) show that  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids and reference samples exhibit similar mesopore diameter distribution (2.07 nm), pore volume ( $0.0054 \text{ cm}^3 \text{ g}^{-1}$ ), and Brunauer-Emmett-Teller (BET) surface area ( $0.9839 \text{ m}^2 \text{ g}^{-1}$ ), indicating both Ni SAs and OVs have no significant effect on the structure of catalysts.

From the powder X-ray diffraction (XRD) patterns of  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids (Fig. 1e) and reference samples (Fig. S4a), the peaks at  $23.1^\circ$ ,  $23.6^\circ$ , and  $24.4^\circ$  are ascribed to the (002), (020), and (200) crystal planes of monoclinic  $\text{WO}_3$  (PDF#83–0950) [41,42]. Meanwhile, it is visible that the above diffraction peaks of  $\text{H}_x\text{WO}_{3-y}$  and  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids (Fig. S4b) are slightly biased toward lower diffraction angles compared to those of pristine  $\text{WO}_3$  and  $\text{Ni}/\text{WO}_3$ , suggesting the distortion and expansion of the lattice after H-spillover process [40]. Furthermore, compared to pristine  $\text{WO}_3$  and  $\text{Ni}/\text{WO}_3$ , the three main vibrational bands at  $711.5$ ,  $262.7$ , and  $800.0 \text{ cm}^{-1}$  in Raman spectra (Fig. S5) of  $\text{H}_x\text{WO}_{3-y}$  and  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids belong to bending vibration of  $\delta(\text{O}-\text{W}-\text{O})$ , stretching vibration of  $\nu(\text{W}-\text{O}-\text{W})$  and  $\text{W}-\text{O}$  stretching of the monoclinic phase, respectively, where OVs leads to peaks shift to lower wavelengths [37,43,44]. Furthermore, according to the Fourier transform infrared (FTIR) spectra (Fig. S6), the absorption peaks of  $1041 \text{ cm}^{-1}$ ,  $795 \text{ cm}^{-1}$ , and  $584 \text{ cm}^{-1}$  can be assigned to the  $\text{W}-\text{O}$ ,  $\text{O}-\text{W}-\text{O}$ , and  $\text{W}-\text{O}-\text{W}$  bonds, respectively [45,46]. The above absorption peaks in  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids are broader compared to those of  $\text{WO}_3$ , indicating that the introduction of more OVs in  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids results in the weaker vibrations of the above bonds [47,48]. According to the UV/Vis-NIR spectra (Fig. 1f and Fig. S7a),  $\text{H}_x\text{WO}_{3-y}$  and  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids show strong light responses in the visible and near-infrared regions, especially  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids which have a strong LSPR peak pinning at around 550 nm. In contrast,  $\text{WO}_3$  and  $\text{Ni}/\text{WO}_3$  only exhibit similar intrinsic absorption below about 480 nm [26,37], which is attributed to the indirect bandgap absorption edge of  $\text{WO}_3$  (around



**Fig. 1.** (a) Schematic diagram of the synthetic process, (b) HRTEM image, (c) EDX elemental mappings, (d) high-resolution HAADF-STEM image, (e) XRD pattern, (f) UV/Vis-NIR absorption spectrum, and (g) EPR spectrum of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids.

2.8 eV)<sup>10</sup>. EPR spectroscopy is performed to further examine the surface OV<sub>s</sub> (Fig. 1g and Fig. S8). The *g* value in WO<sub>3</sub> shows a weak peak at 2.003 from the single electron trapped by OV<sub>s</sub>. Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids show the highest peak compared to references, demonstrating a significant increase in OV<sub>s</sub> concentration in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids.

In addition, other metal SAs decorated on H<sub>x</sub>WO<sub>3-y</sub> including the noble metal Pd/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. S9) and the transition metal Cu/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. S10) are prepared by the same H-spillover process. Detailed characterizations confirm the uniform distribution of metal SAs and the formation of OV<sub>s</sub> on H<sub>x</sub>WO<sub>3-y</sub> supports. Moreover, both Pd/H<sub>x</sub>WO<sub>3-y</sub> hybrids and Cu/H<sub>x</sub>WO<sub>3-y</sub> hybrids have similar structure (Fig. S5b) and light absorption ability (Fig. S7b) as Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids.

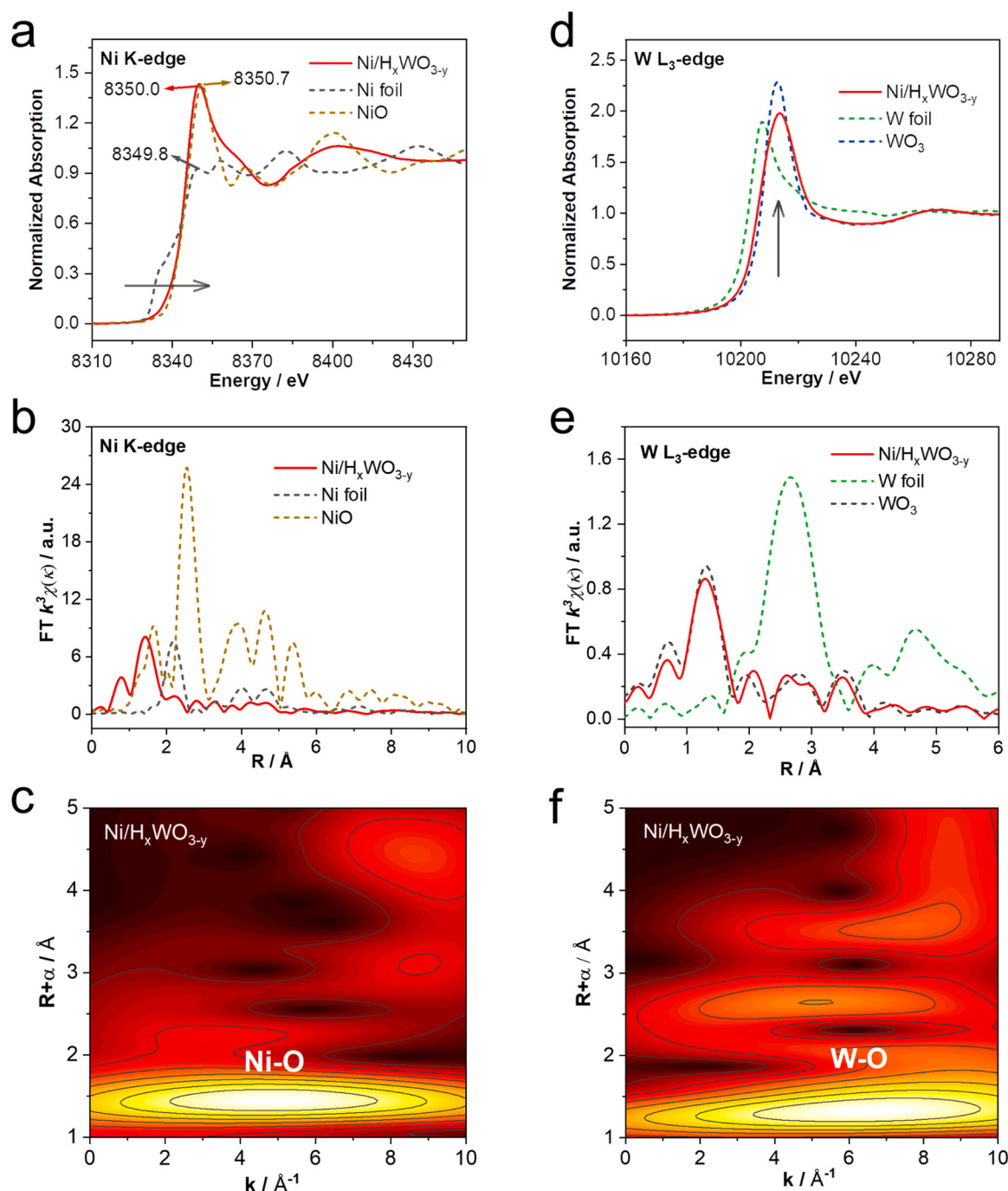
### 3.2. Structural parameters and coordination environment

To explore the fine chemical composition and atomic-level structure of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, we perform X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) analysis. Based on the O 1s XPS spectra (Fig. S11), the peak at 530.65 eV is attributed to lattice oxygen (O<sub>latt.</sub>) in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, whereas other peaks at 531.85 and 532.95 eV are assigned to -OH groups (O<sub>OH</sub>) and -OH<sub>2</sub> groups (O<sub>H2O</sub>), respectively. Compared to WO<sub>3</sub> and Ni/WO<sub>3</sub>, the peak intensities of O<sub>OH</sub> species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and H<sub>x</sub>WO<sub>3-y</sub> significantly enhance after H-spillover process, demonstrating the formation of

W-OH bond. The enhanced W-OH bond concentration after H intercalation absolutely matches the analysis results of Raman and EPR spectra. Furthermore, no Ni<sup>0</sup> peaks can be found in the Ni 2p XPS of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. S12), suggesting Ni species exist in the form of Ni-O coordination rather than Ni NPs. From W 4f XPS spectra (Fig. S13) of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, the peaks at 35.95 and 38.05 eV are attributed to the major W species (W<sup>6+</sup>), while the appearance of the low oxidation state W<sup>5+</sup> is also observed (34.65 and 36.85 eV). In contrast, only W<sup>6+</sup> species are present in pristine WO<sub>3</sub>, suggesting the partial reduction of W<sup>6+</sup> during H-spillover process. The calculation of the XPS peak area of W 4f shows that W<sup>6+</sup> and W<sup>5+</sup> account for 86 % and 14 % of the total W elements, respectively. The average oxidation state of W species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is further calculated to be 5.86, which arises from the OV<sub>s</sub>. Moreover, peaks position of both O 1s and W 4f in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids change to higher binding energies compared to WO<sub>3</sub>, demonstrating that the electron transfers from the H<sub>x</sub>WO<sub>3-y</sub> to Ni SAs, making Ni species in incomplete oxidation state.

To further determine chemical state and atomic coordination structures of Ni and W species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, the XAFS spectra of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and references are acquired at Ni K-edge and W L<sub>3</sub>-edge, respectively. According to X-ray near-edge structure (XANES) spectroscopy (Fig. 2a), the peak location of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids (red line, 8350.0 eV) shifts to higher energy compared to Ni foil (gray line, 8350.7 eV), proving that Ni SAs in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids exhibit electron-deficient features. Moreover, the absorption edge of Ni/





**Fig. 2.** (a) XANES spectra, (b) FT-EXAFS spectra, and (c) WT-EXAFS spectra at Ni K-edge of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and references. (d) XANES spectra, (e) FT-EXAFS spectra, and (f) WT-EXAFS spectra at W L<sub>3</sub>-edge of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and references.

H<sub>x</sub>WO<sub>3-y</sub> hybrids is between NiO (brown line) and Ni foil (black arrow), indicating that the valence state of Ni SAs ranges from 0 to + 2. From the Fourier transformation EXAFS (FT-EXAFS) curves (Fig. 2b) of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and references, the lengths of Ni-O bond and Ni-Ni bond are 1.66 Å and 2.18 Å, respectively. No Ni-Ni bonds are found in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, proving that Ni atoms are atomically dispersed and coordinated with O atoms (1.45 Å) in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. This corresponds to the analysis of HADDF-STEM images (Fig. 1b). Wavelet transform (WT)-EXAFS oscillations are carried out in both K and R spaces in order to better observe the atomic conformation of Ni species over Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. The WT-EXAFS contour plot of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. 2c) reveals Ni-O coordination through a maximum of around 1.45 Å. No typical Ni NPs (Fig. S14a; 2.18 Å) and NiO (Fig. S14b;

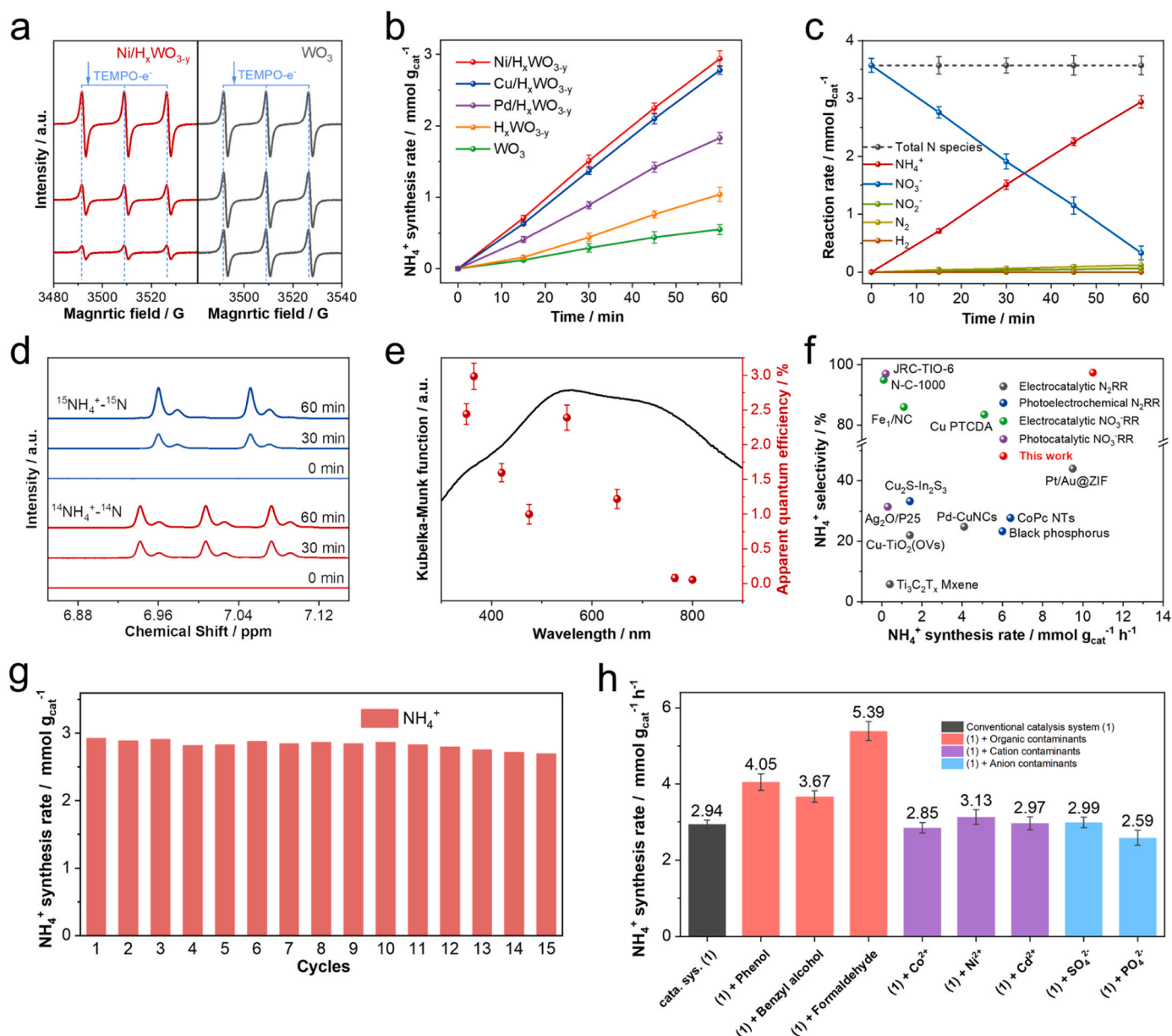
2.60 Å) signals are observed in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. In addition, the O coordination mode of Ni species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is also further determined by Ni K-edge EXAFS fitting analysis (Fig. S14c-d and Table S1). Furthermore, W L<sub>3</sub>-edge XANES spectra (Fig. 2d) show that W peak intensity (red line) lies between WO<sub>3</sub> (blue line) and W foil (green line), reflecting that the valence range of W species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is between 0 and + 6. It can be observed from the FT-EXAFS curves (Fig. 2e) that the intensity of the first shell layer coordination peak of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids decreases and shifts 0.03 Å toward the lower R, which is attributed to the local atomic alignment change [49]. The abundant OV's reduce the coordination number of W species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and shorten the exposed W-O bond length to enhance electron transfer [50]. Furthermore, the coordination mode and

bonds length (1.32 Å) of W in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids are also determined by WT-EXAFS oscillations (Fig. 2f and Fig. S15a-b) and W L<sub>3</sub>-edge EXAFS fitting analysis (Fig. S15c-d and Table S2). Similarly, the XAFS spectra of Pd/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. S16, Fig. S17, Table S2, and Table S3) and Cu/H<sub>x</sub>WO<sub>3-y</sub> hybrids (Fig. S18 and Table S4) indicate that the configurations of metal SAs and OVs are also successfully obtained in Pd/H<sub>x</sub>WO<sub>3-y</sub> hybrids and Cu/H<sub>x</sub>WO<sub>3-y</sub> hybrids.

### 3.3. The charge carrier dynamics and band structures of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids

To elucidate the roles of Ni SAs coupled OVs in enhancing photo-generated electron dynamics, the photochemical properties and photoluminescence spectra of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and reference samples are investigated. Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids have the largest photocurrent and a

periodic on/off response compared to the photocurrent generated by reference samples (Fig. S19a), demonstrating that Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids have the highest photogenerated carrier separation efficiency. The Nyquist plots of the electrochemical impedance spectra (EIS; Fig. S19b) show that Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids display an obviously smaller semicircle diameter than reference samples, indicating a smaller resistance and an increased charge transfer capacity of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. Moreover, compared to reference samples, Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids show a weaker band-to-band emission peak at 580 nm in the photoluminescence (PL) spectra (Fig. S19c) owing to the suppression of radiative recombination pathway for the photogenerated carriers [51]. Furthermore, we obtain carrier lifetime by analyzing time-resolved PL (TRPL) spectra (Fig. S19d) to derive charge-transfer kinetics. Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids have a longer  $\tau$  (0.10 ns) than WO<sub>3</sub> (0.08 ns), which reflects that photogenerated electrons tend to concentrate in the dual active sites for NH<sub>3</sub> synthesis rather



**Fig. 3.** (a) EPR spectra for TEMPO showing the reactive species of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids and WO<sub>3</sub>. (b) Time-dependent concentration change of NH<sub>4</sub><sup>+</sup>. (c) Time-dependent concentration change of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, N<sub>2</sub>, and H<sub>2</sub> over Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. (d) <sup>1</sup>H NMR spectra of time-dependent concentration change of NH<sub>4</sub><sup>+</sup> using <sup>15</sup>NO<sub>3</sub><sup>-</sup> and <sup>14</sup>NO<sub>3</sub><sup>-</sup> as the NO<sub>3</sub><sup>-</sup> source. (e) AQEs (red spots) of NO<sub>3</sub><sup>-</sup> reduction under monochromatic light irradiation are calculated against UV/Vis-NIR absorption spectrum. (f) Comparison of the selectivity and rates of NH<sub>4</sub><sup>+</sup> synthesis through different methods under ambient conditions [52–62]. (g) Cycle test of photocatalytic NH<sub>4</sub><sup>+</sup> synthesis by NO<sub>3</sub><sup>-</sup> reduction on Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. (h) NH<sub>4</sub><sup>+</sup> synthesis rates after the addition of different pollutants (organic, cationic, and anionic pollutants).

than recombine with holes. To verify the ability for generating active radicals on Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, we perform EPR experiments utilizing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the trapping reagent (Fig. 3a and Fig. S20). The TEMPO signals on Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids diminish rapidly under light irradiation compared to that on pristine WO<sub>3</sub>, indicating that more photoexcited electrons can be produced and consumed over Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. Additionally, the signals of another trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) in light irradiation are much stronger than those in dark (Fig. S21), suggesting that Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids can produce more O<sub>2</sub><sup>•-</sup> and •OH compared to reference samples. Meanwhile, for Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, the quantities of the generated O<sub>2</sub><sup>•-</sup> and •OH under visible light irradiation are obviously stronger than those in dark condition. In conclusion, the introductions of OVs and Ni SAs in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids greatly enhance the separation efficiency of photogenerated electron-hole pairs. According to (ahv)<sup>2</sup> versus (hv) (Fig. S22a), the calculated bandgap of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is 1.28 eV, which is significantly less than the bandgaps of WO<sub>3</sub> (2.57 eV), Ni/WO<sub>3</sub> (2.50 eV), and H<sub>x</sub>WO<sub>3-y</sub> (1.66 eV). Mott-Schottky measurement (Fig. S22b) is conducted from the electrochemical approach to determine the position of the flat band potential. All photocatalysts have positive slope, which is characteristic of n-type semiconductors. Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids show the lowest flat band potential (Fermi level, E<sub>f</sub>), corresponding to the lowest surface work function. This enables efficient transfer of electrons from H<sub>x</sub>WO<sub>3-y</sub> to Ni SAs. Furthermore, based on the valence band XPS (VB-XPS) spectra (Fig. S22c), VBs of WO<sub>3</sub> and Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids are estimated to be 2.70 and 2.45 eV, respectively. Notably, VB spectrum of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids clearly shows the existence of a defect band, which is derived from local electron induction in the d orbitals of W<sup>5+</sup> species. Based on the electronic band structures vs vacuum level (Fig. S22d) [23], the conduction band position of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is much lower than E<sub>f</sub> due to the presence of defect bands, representing the characteristic of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids with degenerate semiconductors.

### 3.4. Photocatalytic performance of NH<sub>3</sub> synthesis from NO<sub>3</sub><sup>-</sup>

After obtaining the configuration of OVs and Ni SAs, we further explore the performance of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids in photocatalytic NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub> (NO<sub>3</sub><sup>-</sup> + 8e<sup>-</sup> + 9H<sup>+</sup> → NH<sub>3</sub> + 3H<sub>2</sub>O) at ambient conditions, which is conducted in 50 mL of KNO<sub>3</sub> solution (10 mg/L of NO<sub>3</sub><sup>-</sup>) with 10.0 % ethylene glycol (EG) as the hole sacrificial agent under full spectrum illumination. The presence of EG has no effect on the quantitative detection of NH<sub>4</sub><sup>+</sup> using Nessler's reagent (Fig. S23), <sup>1</sup>H NMR spectra (Fig. S24), and cation chromatography (Fig. S25). As shown in Fig. 3b, small amounts of NH<sub>4</sub><sup>+</sup> are generated on commercial WO<sub>3</sub> (0.55 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). The efficiency of NH<sub>3</sub> synthesis on H<sub>x</sub>WO<sub>3-y</sub> with OVs is initially improved (1.04 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). Notably, the simultaneous introduction of OVs and SAs (i.e., Ni/H<sub>x</sub>WO<sub>3-y</sub>, Cu/H<sub>x</sub>WO<sub>3-y</sub>, and Pd/H<sub>x</sub>WO<sub>3-y</sub>) can dramatically improve the activity of NH<sub>3</sub> synthesis. Among them, Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids achieve the highest NH<sub>3</sub> yield of 2.94 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which is 2.82, 2.67, and 5.35 times higher than that of H<sub>x</sub>WO<sub>3-y</sub>, Ni/WO<sub>3</sub> (Fig. S26), and WO<sub>3</sub>, respectively, highlighting the important role of OVs and SAs. Specifically, with the increase of reaction time, NH<sub>4</sub><sup>+</sup> yield rate increases and reaches the maximum after 60 min (Fig. 3c) with NH<sub>4</sub><sup>+</sup> synthesis selectivity of 98.26 %, while the concentration of NO<sub>3</sub><sup>-</sup> gradually decreases. Moreover, few by-products (NO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>) are produced, confirming that NO<sub>3</sub><sup>-</sup> is mainly converted to NH<sub>4</sub><sup>+</sup> in photocatalytic NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub>. Meanwhile, the amount of total nitrogen in the reaction mixture remains stable and the trace production of by-products indicates that the five-electron-transfer synthesis of nitrogen and the water-cracking side reaction are effectively suppressed. Furthermore, to eliminate the potential effects of other nitrogen-containing substances, we conduct blank control group experiments in the absence of catalyst and NO<sub>3</sub><sup>-</sup> (Fig. S27), which indicate that no NH<sub>4</sub><sup>+</sup> is generated. Moreover, <sup>15</sup>N and <sup>14</sup>N isotopic labeling experiments are also performed, where NO<sub>3</sub><sup>-</sup> and the produced

NH<sub>4</sub><sup>+</sup> are detected by IC (Fig. S28) and <sup>1</sup>H NMR (Fig. 3d and Fig. S29) technologies. K<sup>14</sup>NO<sub>3</sub> and K<sup>15</sup>NO<sub>3</sub> solutions are used as N sources. The <sup>1</sup>H NMR spectra of the reaction solution after photocatalytic reduction of K<sup>15</sup>NO<sub>3</sub> show a clear double peak typical of <sup>15</sup>NH<sub>4</sub><sup>+</sup> (7.05 and 6.96 ppm) and no triple peak typical of <sup>14</sup>NH<sub>4</sub><sup>+</sup> (7.07, 7.01, and 6.94 ppm). Both <sup>15</sup>NH<sub>4</sub><sup>+</sup> and <sup>14</sup>NH<sub>4</sub><sup>+</sup> are quantified by comparing the peak areas of external standards (maleic acid, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>; Fig. S29). Based on the similar rates for <sup>14</sup>NO<sub>3</sub><sup>-</sup>/<sup>15</sup>NO<sub>3</sub><sup>-</sup> reduction and <sup>14</sup>NH<sub>4</sub><sup>+</sup>/<sup>15</sup>NH<sub>4</sub><sup>+</sup> production (Fig. 3d and Fig. S28), the generated NH<sub>4</sub><sup>+</sup> is confirmed to be directly sourced from NO<sub>3</sub><sup>-</sup> feedstock rather than other N-containing species. The apparent quantum efficiencies (AQEs) of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids are evaluated under different monochromatic light irradiation (Fig. 3e) to investigate light utilization efficiency. The AQEs show essentially the same optical absorption trends in the visible and near-infrared regions as the Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. It can be seen that the AQE reaches 2.39 % at 550 nm, which indicates that the excitation of H<sub>x</sub>WO<sub>3-y</sub> mainly comes from LSPRs effect induced by OVs in the Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids.

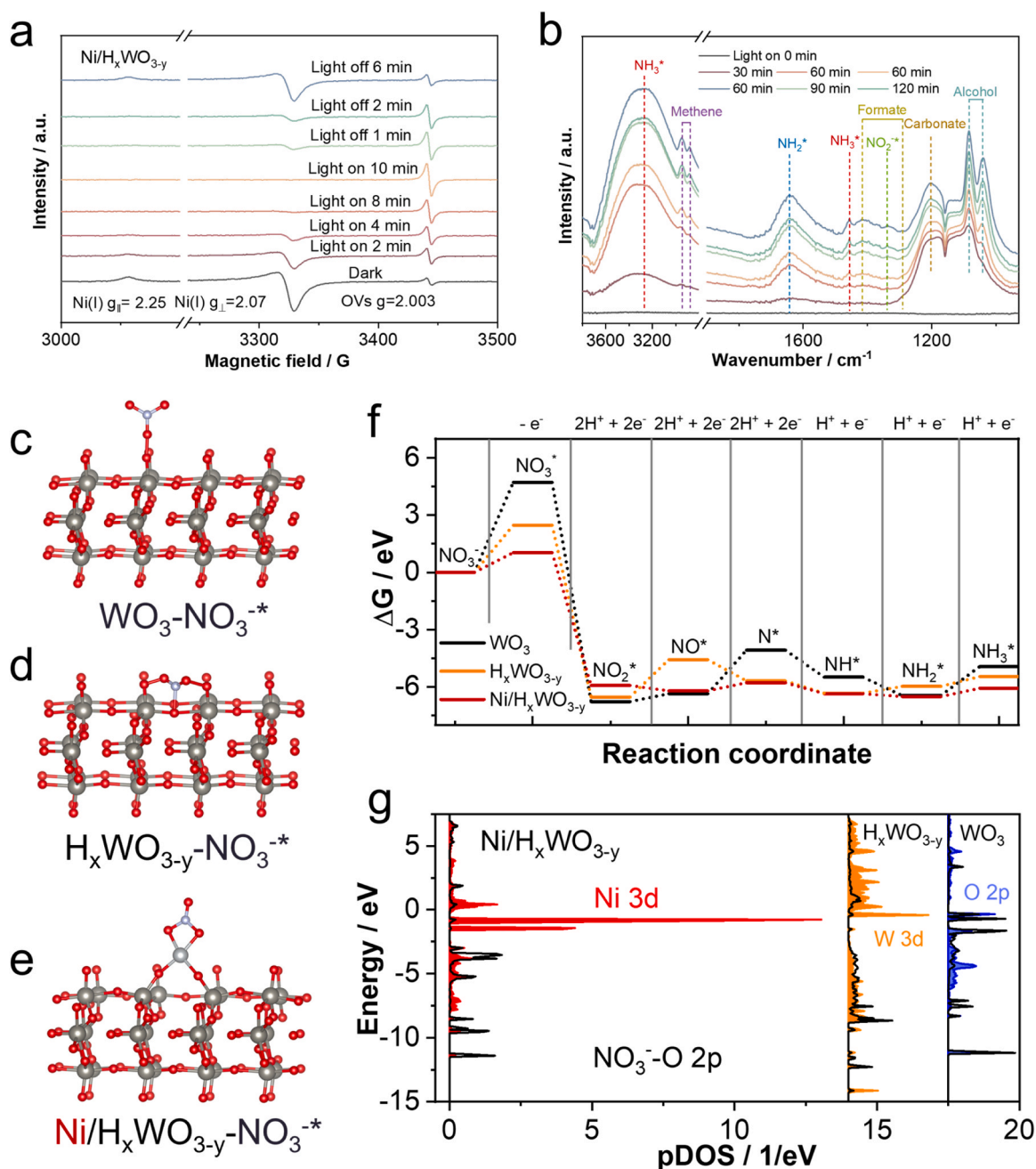
As the reaction parameters directly affect the catalytic efficiency, an in-depth modification of the NO<sub>3</sub><sup>-</sup> concentration and catalyst dosage are performed to further enhance the catalytic performance. The best reaction kinetics of NH<sub>3</sub> synthesis achieve in NO<sub>3</sub><sup>-</sup> concentration of 60.0 mg/L (Fig. S30) and the catalyst dosage of 1.0 mg (Fig. S31). Ultimately, the optimized reaction conditions resulted in a photosynthesis rate of 10.5 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> over Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. More importantly, compared to other NH<sub>3</sub> synthesis pathways under ambient conditions (Fig. 3f), the NH<sub>3</sub> yield and selectivity by photocatalytic NO<sub>3</sub><sup>-</sup> reduction on Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids are still in a relatively leading position among photocatalytic NH<sub>3</sub> synthesis fields, even surpassing some electrocatalytic NH<sub>3</sub> synthesis work despite the fact that electrocatalytic process delivers a much higher input power [52–65]. In addition, the stability of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids is further investigated (Fig. 3g). The activity of NH<sub>3</sub> synthesis only shows a slightly downward trend during 15 cycle tests, confirming the photostability of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. Moreover, the XRD, Raman, XPS, and UV–vis spectra (Fig. S32) after reaction remain almost unchanged, also confirming its application stability.

Considering that the real wastewater not only contains NO<sub>3</sub><sup>-</sup> but also contains various organic pollutants, they can also be served as pore sacrificial agents in the photocatalytic process. To simulated wastewater, we add phenol, benzyl alcohol, and formaldehyde as potential contaminants in photocatalysis system (Fig. 3h). We find that NH<sub>3</sub> yield rate has no decrease in simulated wastewater, indicating the potential of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids in actual organic wastewater. Meanwhile, cation (Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>) and anion (SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>) contaminants in real wastewater have few effects on the stability of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids. It demonstrates that Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids with Ni SAs and OVs have significant scientific implications in the field of environmental remediation and energy conversion.

### 3.5. Proposed mechanism and DFT calculations

Based on the key roles of OVs and Ni SAs of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids, we further perform in situ EPR to verify the active sites of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids in photocatalytic NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub>. Firstly, in the time-dependent in situ EPR spectroscopy measurements (Fig. 4a), comparing the EPR spectrum of H<sub>x</sub>WO<sub>3-y</sub> (Fig. S33), the peak at g = 2.003 can be assigned to the OVs, while the signals at g<sub>||</sub> = 2.25 and g<sub>⊥</sub> = 2.07 indicate the formation of Ni(I) species in Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids [66]. The normalized intensities of OVs and Ni(I) are further computed to clearly depict the dynamics of each site (Fig. S34). Interestingly, the normalized intensity of OVs gradually increases after irradiation, while the normalized intensity of Ni(I) decreases after enrichment of electrons to Ni (0). They gradually reach the equilibrium intensity after 10 min [67]. Finally, the normalized intensities of OVs and Ni(I) almost return to the initial levels in 6 min after turning off the light, demonstrating both OVs and Ni SAs of Ni/H<sub>x</sub>WO<sub>3-y</sub> hybrids are the dual active sites in





**Fig. 4.** (a) In situ EPR spectra at 77 K (cooled by liquid nitrogen), and (b) in situ DRIFTS in photocatalytic  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  over  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids. Adsorption models of  $\text{NO}_3^{*-}$  on (c)  $\text{O-WO}_3$ , (d) OV site of  $\text{H}_x\text{WO}_{3-y}$ , and (e) Ni site of  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids, respectively. (f) Free-energy diagram for photocatalytic  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  over  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids. (g) pDOS plots of  $\text{NO}_3^{*-}$  adsorption on  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids,  $\text{H}_x\text{WO}_{3-y}$ , and  $\text{WO}_3$ .

photocatalytic  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ . Based on the above analysis, we can conclude that photogenerated electrons of  $\text{H}_x\text{WO}_{3-y}$  are successfully trapped by OV and Ni SAs in light irradiation and the initial state is restored after turning off the light. Thus,  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids cannot be easily corroded in  $\text{NO}_3^-$  reduction under light irradiation. Moreover, in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) technique is performed to detect the key molecular intermediates and clarify the reaction mechanism (Fig. 4b). The positive peaks at  $1339 \text{ cm}^{-1}$  are attributed to  $\text{NO}_2^*$  intermediates, while the peaks at  $1646 \text{ cm}^{-1}$  are assigned to  $\text{NH}_2^*$ . It is evident that the peak intensities of  $\text{NH}_4^*$  ( $3270$  and  $1453 \text{ cm}^{-1}$ ) rise with the increase of reaction time, which is consistent with the reaction path of  $\text{NH}_3$  synthesis by  $\text{NO}_3^-$  reduction. Meanwhile, the EG in the effluent actually acts as a pore sacrificial agent in the catalytic system, thus, the pathway of

EG-catalyzed oxidation is also explored by DRIFTS technique. With increasing reaction time, we can observe the formation and accumulation of methane ( $2948$  and  $2877 \text{ cm}^{-1}$ ), alcohol ( $1085$  and  $1040 \text{ cm}^{-1}$ ), formate ( $1418$  and  $1291 \text{ cm}^{-1}$ ), and carbonate ( $1203 \text{ cm}^{-1}$ ), which can be attributed to the EG catalytic oxidation. Based on the detection of reaction process by in situ DRIFTS, we deduce pathways for  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  including the transfer of eight electrons and nine protons ( $\text{NO}_3^- + 8\text{e}^- + 9\text{H}^+ \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$ ).

To prove the above conclusion, we further calculate the relative free energies of the intermediates on  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids and reference samples in  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  by DFT calculations with the assistance of computational hydrogen electrode model [68]. The stable structural configurations of  $\text{WO}_3$ ,  $\text{H}_x\text{WO}_{3-y}$ , and  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids are shown in Fig. 4c-e. When OV are introduced to  $\text{WO}_3$ , the adsorption site of

$\text{NO}_3^-$  transfers from O atom of  $\text{WO}_3$  to OV of  $\text{H}_x\text{WO}_{3-y}$ . For  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids, Ni SAs are the adsorption site of  $\text{NO}_3^-$ . The adsorption energies of  $\text{NO}_3^-$  on Ni SA- $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids (1.28 eV) and OV- $\text{H}_x\text{WO}_{3-y}$  (2.47 eV) are significantly lower than those on O- $\text{WO}_3$  (4.72 eV), indicating that the dual active sites in  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids are more favorable for  $\text{NO}_3^-$  adsorption (Fig. 4f). Notably,  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids greatly reduce the energy of the rate-determining steps for  $\text{H}_x\text{WO}_{3-y}$  ( $\text{NO}_2^* \rightarrow \text{NO}^*$ ), suggesting that Ni SAs can kinetically accelerate the deoxygenation process. In addition, the projected density of states (pDOS) between the electron orbitals of the different adsorption sites and the 2p orbitals of  $\text{NO}_3^-$ -O (Fig. 4g) is used to probe the electronic band structure. By comparing the overlap between the Ni 3d - O 2p, W 3d - O 2p, and O 2p - O 2p, the p-d orbital hybridizations of OV and Ni SAs dual active sites and  $\text{NO}_3^*$  are obviously stronger than that of  $\text{WO}_3$ . Therefore, electrons can be easily transferred to the coordination O of  $\text{NO}_3^*$  through the Ni-O and W-O bonds. Moreover, OV and Ni SAs significantly increase the density of states near the  $E_f$  level, which facilitates the electron conductivity and electron transfer ability[69].

#### 4. Conclusion

In summary, we prepare  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids containing abundant OV and Ni SAs to efficiently and highly selective reduce  $\text{NO}_3^-$  to  $\text{NH}_3$  by photocatalysis.  $\text{Ni}/\text{H}_x\text{WO}_{3-y}$  hybrids have highly selective and efficient photocatalytic  $\text{NH}_3$  synthesis from  $\text{NO}_3^-$  reduction. The synergetic effect of OV and Ni SAs plays a key role in  $\text{NH}_3$  synthesis, that is, (1) OV acts as adsorption sites of  $\text{NO}_3^-$  and transfer photogenerated electron and adsorbed  $\text{NO}_3^-$  to Ni SAs by LSPRs effect; (2) Ni SAs are mainly responsible for  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ . Meanwhile, the strong hybridization of 3d-2p orbitals between Ni SAs and  $\text{NO}_3^-$ -O further promotes the electron transfer from Ni SAs to  $\text{NO}_3^-$ . And the induction of Ni SAs effectively reduce the free energy of the rate-limiting step ( $\text{NO}_2^* \rightarrow \text{NO}^*$ ) of  $\text{H}_x\text{WO}_{3-y}$ . This study provides a promising strategy for exploring metal SAs/plasmonic semiconductor with dual active sites for the pollutants treatment in wastewater.

#### CRedit authorship contribution statement

Yunlong Wang, Haibo Yin, and Xiaoguang Zhao contributed equally to this work. Yunlong Wang, Haibo Yin, and Xiaoguang Zhao proposed, designed and performed the experiments, and analyzed data. All authors discussed, commented on and revised the manuscript.

#### Declaration of Competing Interest

The authors declare no competing financial interest.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123266](https://doi.org/10.1016/j.apcatb.2023.123266).

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